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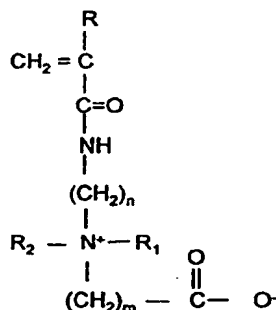
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(54) Title: WATER-SOLUBLE, HYDROLYTIC-STABLE AMPHOTERIC MONOMER AND POLYMERS THEREFROM



(57) Abstract

This invention relates to a monomer having formula (I) wherein: R is hydrogen or C<sub>1</sub> to C<sub>4</sub> alkyl, typically hydrogen or methyl; R<sub>1</sub> and R<sub>2</sub> are independently C<sub>1</sub> to C<sub>18</sub> alkyl, typically C<sub>1</sub> to C<sub>4</sub> alkyl, more typically methyl or ethyl; n is 2 to 10, typically 2, 3, or 4; and m is 1 to 10, typically 1, 2, 3, or 4. This invention also relates to a homopolymer derived from the above monomer and to copolymer of one or more of the above monomers and another monomer.

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**Water-Soluble, Hydrolytic-Stable Amphoteric Monomer  
and Polymers Therefrom**

5

**Field of the Invention**

This invention relates to a monomer that is water-soluble and hydrolytically stable and to polymers prepared therefrom which are particularly useful conditioning agents, e.g. in personal care compositions such as shampoos.

**Background of the Invention**

Polyquaternary polymers have been used in a variety of industrial formulations, including cosmetic formulations. However, to date, one of the most important applications is their use in hair and skin formulations, including hair shampoos and hair conditioning products.

Hair shampoos generally are formulated with highly effective synthetic surfactants, such as anionic surfactants, that clean the hair. The anionic surfactants not only remove the dirt and soil from the hair but concomitant therewith, they unfortunately also remove all of the sebum naturally present on the surface of hair fibers. As a result, shampoo compositions containing these surfactants leave the hair with an undesirable harsh, dull and dry touch or feel, usually called "creak", after the hair is shampooed and then rinsed with water.

Furthermore, thoroughly cleansed hair also is extremely difficult to comb, in either the wet or the dry state, because the individual hair fibers tend to snarl, kink and interlock with each other. If the hair is incompletely dried, such as hair dried with a towel, the hair has poor brushing properties, and after complete drying, the hair does not set well.

The combing or brushing property of the hair remains poor and in low humidity atmospheres, the hair has undesirable electrostatic properties, causing the hair to "fly away", thereby reducing the brushing properties of the hair. The unsatisfactory combing or brushing property of hair  
5 immediately after shampooing also causes hair damage, such as split ends or hair breakage. In addition, shampooing of hair reduces the natural luster and resiliency of the hair, thereby giving the hair a dull appearance.

Thus, shampoos usually neither aid in the detangling of wet  
10 hair nor impart any residual conditioning benefits to dry hair, such as manageability or styleability of hair sets. The overall unsatisfactory condition of the shampooed hair necessitates the use of a conditioning composition to improve these undesirable physical characteristics. The conditioning composition may be applied separately from the hair  
15 shampoo as a post-shampoo treatment of the hair or may be incorporated into the hair shampoo. However, because many of the most widely used products for treating hair contain anionic surfactants and as explained herein below, conditioning compositions usually contain cationic polymers as the active ingredient, and because cationic material are usually  
20 inactivated by reaction with anionic surfactants, it is customary to employ conditioner containing cationic materials as a separate composition, such as post- shampoo rinse, separately applied.

The conditioning agents that have been utilized in the prior art are cationic compounds such as cationic surfactants and cationic  
25 polymers. They render the hair more manageable. For example, the wet combing problem discussed herein above is solved by the use of these conditioners which coat the hair shaft and cause the individual hair shafts in a tress to resist tangling and matting because of the conditioner residue retained on the shaft. The ability of these cationic compounds to  
30 absorb or react with the keratinous material of the hair makes them the

most desirable compounds for imparting the desired improvement in wet hair detangling and dry hair manageability. Many of these cationic compounds are polyquaternary polymers prepared from monomers with an ester functionality, for example, acrylate or methacrylate types, as a  
5 comonomer.

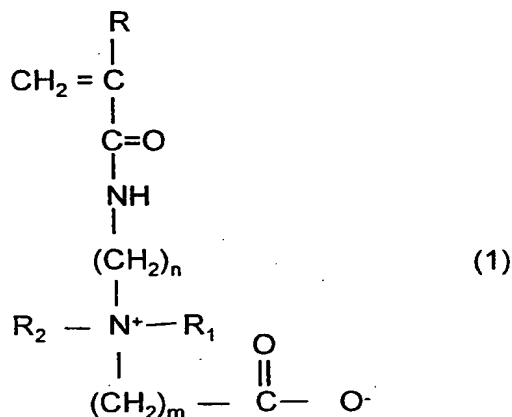
Chemical Abstracts, 109:191452 is an abstract of U.S.S.R. Patent 1,399,306 to A.M. Leonova et al., for a Method of Producing Polymer Flocculant. The polymer of the title is produced by polymerizing dimethylaminoethyl methacrylate salts in water in the presence of a  
10 radical initiator. The product of the polymerization thus contains ester functionality and is described as gel-like.

Although they are useful, these polyquaternary polymers containing esters have several disadvantages associated therewith. For example, they tend to be hydrolytically unstable to the extent that the  
15 formulation must avoid conditions conducive to hydrolysis during formulation, such as acidic or basic conditions and higher temperatures such as temperatures greater than about 30°C. Under these conditions, they decompose and catalytically hydrolyze as a result of contact with water, including trace amounts thereof, into the methacrylic acid and the  
20 corresponding dialkylalkanolamine, resulting in significant lowering of viscosity and concomitant reduction in beneficial properties.

Moreover, the esters used heretofore lack hydrogen bonding capability with skin protein or hair keratin; consequently the hair substantivity, when applied, is not satisfactory.

**Summary of the Invention**

This invention relates to a monomer having the formula:



wherein:

R is hydrogen or C<sub>1</sub> to C<sub>4</sub> alkyl, typically hydrogen or methyl;

R<sub>1</sub> and R<sub>2</sub> are independently C<sub>1</sub> to C<sub>18</sub> alkyl, typically C<sub>1</sub> to C<sub>4</sub> alkyl, more typically methyl or ethyl;

10 n is 2 to 10, typically 2, 3, or 4; and m is 1 to 10, typically 1, 2, 3 or 4.

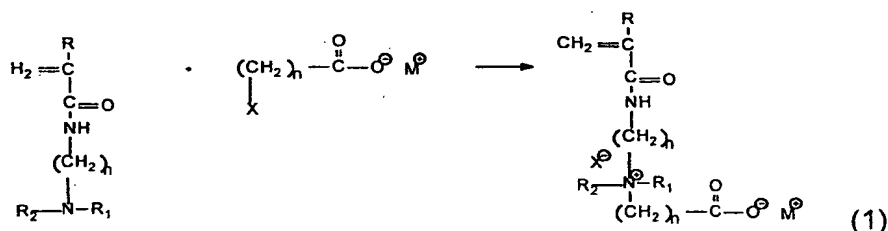
This invention also relates to a homopolymer derived from the above monomer and to copolymer of one or more of the above monomers and another monomer. This invention also relates to personal care compositions comprising such polymers and to methods of making  
15 and using same in guar compositions.

**Detailed Description of the Invention**

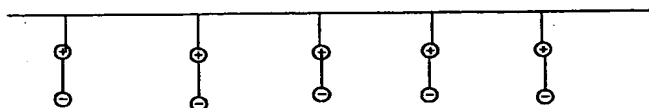
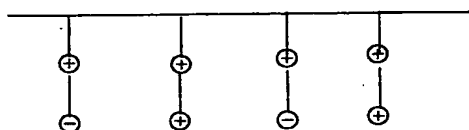
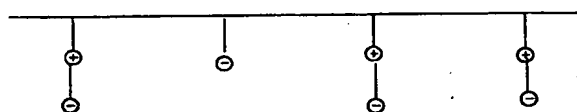
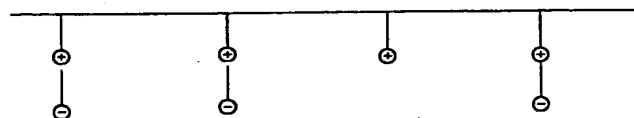
The water-soluble amphoteric monomer is synthesized by reacting a monomer bearing an amino group with an alkyl halide bearing  
20 a carboxylate group. The resulting monomer is water-soluble but hydrolytic-stable. The vinyl functionality adjacent to an amide linkage thus enables the monomer with high reactivity for polymerization as well

as providing hydrolytic-stability even in the monomer phase. Due to its water-solubility and reactivity, thus it can undergo homopolymerization as well as copolymerization with a variety of water-soluble monomers in water system to generate numerous new polymers. The resulting polymers would contain amphoteric functionality as well as anionic (with acrylic acid, methacrylic acid, AMPS etc.) or cationic (with many cationic monomers commercially available) or a mixture of all three "functionalities". The betaine-type amphoteric polymer (i.e. with carboxylate functionality) is pH dependent thus it could become cationic at low pH. Also, the amphoteric would provide mildness and better compatibility with anionic/cationic surfactants. For example, the incorporation with this amphoteric monomer to a cationic polymer will show higher anionic surfactant compatibility. The synthesis of the monomers of formula 1 is depicted below:

15



Homopolymerization and copolymerization of the above monomers are easily carried out in water via standard free radical polymerization. A variety of co-monomers can be used such as vinyl pyrrolidone, acrylamide, acrylic acid, vinyl acetate, methacrylic acid, AMPS, and many cationic monomers (e.g. dimethylaminopropyl(meth)acrylamide and its methyl chloride/methyl sulfate quaternary versions). Thus a variety of new polymers can be being made as illustrated immediately below.

**omopolymer****Copolymers**

5                    Examples of the polymers derived from a monomer of this invention and at least one other co-monomer include:

copolymer(VP/AP)

copolymer (AM/AP)

copolymer (MAPTAC/AP)

10                   copolymer (MES/AP)

terpolymer (VP/AP/VA)

terpolymer (VP/AP/MAPTAC)

terpolymer (VP/AP/MES)



terpolymer (VP/AP/Diquat)

terpolymer (AM/AP/MES)

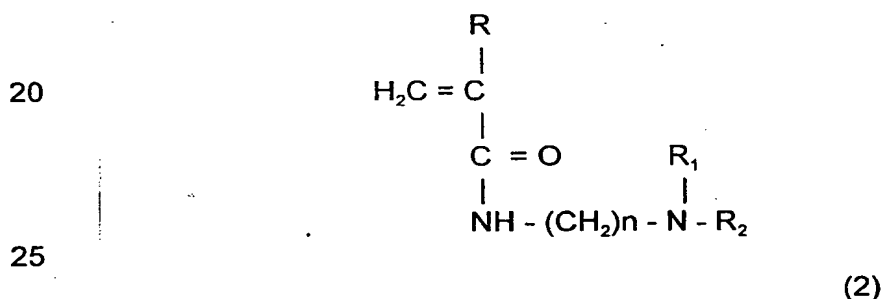
terpolymer (VP/AP/K-AMPS)

terpolymer (VP/AP/BEM)

- 5 wherein the monomer labels are as described in the examples set forth below.

Many of the polymers thus synthesized were examined for compatibility with several anionic surfactant systems currently being used in a shampoo formulation. The results showed that incorporation with the  
 10 amphoteric monomer to a cationic polymer would enhance compatibility with the anionic surfactants. This could indicate that the polymers would be useful as a conditioning agents for personal care applications. The presence of an amphoteric polymer would enhance mildness of the formulation.

- 15 The quaternized monomer of Formula 1 is prepared by reacting an amino alkyl (meth)acrylamide of the formula:



- with sufficient amounts of quaternizing agent  $\text{X}-(\text{CH}_2)_n - \text{COOM}$  wherein X is chlorine or bromine and M is sodium, potassium or ammonium, to  
 30 form the compound of Formula 1 under conditions effective for said quaternization. Preferred quaternizing agents include the sodium potassium, and/or ammonium salts of chloro- or bromo-acetic acid, and/or alpha- or beta-/chloro- or bromo-propionic acid. The reaction is

preferably conducted in an inert solvent such as water, and the reaction is conducted at temperatures ranging from about room temperature to about 120°C. The salt M-X will be produced as a by-product of the quaternizing reaction. It may be desirable to remove the salt, e.g. by ion  
5 exchange, but for typical applications, removal of the salt will not be necessary or desirable.

The homopolymers of the present invention are prepared by subjecting the monomer of Formula 1 to polymerization, and especially free radical polymerization. The reaction is conducted in an oxygen-free  
10 environment, such as in the presence of an inert gas (e.g., helium, argon and the like), or nitrogen. The polymerization is carried out in an inert solvent, preferably methanol or ethanol and most preferably water.

Polymerization is initiated by adding a polymerization initiator. The initiators utilized are the usual free radical initiators.  
15 Examples include organic peresters (e.g., t-butyl peroxy-pivalate, t-amyl peroxy-pivalate, t-butyl peroxy- $\alpha$ -ethylhexanoate, and the like); organic azo compounds (e.g. azobisamidinopropanehydrochloride, azobisisobutyronitrile, azobis-2,4-dimethylvaleronitrile, and the like); inorganic and organic peroxides, (e.g., hydrogen peroxide, benzyl  
20 peroxide, and butyl peroxide and the like), and redox initiator systems, e.g. those having oxidizing agents, such as persulfates (such as ammonium or alkali metal persulfate, and the like), chlorates and bromates (including inorganic or organic chlorates and/or bromates), reducing agents, such as sulfites and bisulfites (including inorganic and/or  
25 organic sulfites or bisulfites) oxalic acid, and ascorbic acid, and combinations thereof. The preferred initiators are water soluble. The most preferred initiators are sodium persulfate and azobisamidinopropanehydrochloride. Alternatively, initiation of polymerization can be instituted by irradiation with ultra-violet light. The  
30 amount of initiator utilized is in general a sufficient amount to effect

initiation of polymerization. Preferably they are present in amounts ranging from about 0.001 to about 10% by weight of monomer and more preferably less than about 0.5% by weight based on the total weight of the monomer, and most preferably from about 0.005 to about 0.5% by weight based upon the weight of the monomer. The initiator is added in the polymerization either continuously or in incremental additions. The continuous or incremental addition of the initiator promotes the polymerization reaction. It is also essential to insure high molecular weight polymer. It has been found that repeated contact of unreacted monomers with fresh initiator, particularly during the final stages of reaction when monomer concentration is greatly reduced, drives the reaction to completion. The gradual or incremental addition also promotes more efficient and conservative use of initiator while permitting a shorter overall reaction time.

The polymerization is conducted under reaction conditions effective to polymerize the monomer of Formula 1 under an oxygen free atmosphere. Preferably, the reaction is conducted at a temperature ranging from about 30°C to about 100°C and more preferably from about 60°C to about 90°C. The oxygen free atmosphere is maintained for the duration of the reaction, for example, the nitrogen purging is maintained throughout the reaction. The continuous purging of the reaction by constant ebullition of inert gas maintains the oxygen free atmosphere.

The polymers of this invention will find use in personal care compositions and/or detergents. Such compositions are those which are intended to accomplish a beneficial result when placed in contact with hair or skin. Among the personal care compositions within the contemplation of this invention are shampoos (which typically contain an anionic surfactant), hair conditioners, skin or hair moisturizers and skin cleansers. Among the detergent compositions are those intended for use

as hard surface cleansers wherein the polymer may reduce deposition onto hard surfaces.

The homopolymer produced by the process described herein may be formulated into a hair conditioning composition. It is the active conditioning ingredient in the formulation and is present in hair conditioning effective amounts. The product is preferably present in an amount ranging from about 0.5% to about 5% by weight of the composition. Preferably, the product is present in an amount ranging from about 1% to about 4% by weight of the composition, and more preferably from about 1% to about 2.5% by weight of the composition.

In hair conditioning formulations the homopolymer produced by the present process is present in the hair conditioning composition in association with a cosmetic vehicle. The vehicle of the present composition is predominantly water, but organic solvents also can be included in order to facilitate manufacturing of the composition or to provide esthetic properties to the compositions, such as viscosity control. Suitable organic solvents include the lower alcohols, like ethyl alcohol and isopropyl alcohol; glycol ethers, e.g. 2-butoxyethanol ethylene glycol monoethyl ether; propylene glycol and diethylene glycol monoethyl ether or monomethyl ether, and mixtures thereof. These organic solvents can be present in the clear hair conditioning composition of the present invention in an amount from about 1 to about 50% by weight and in particular from about 5% to about 25% by weight relative to the total weight of the composition.

The pH of the composition of the present invention ranges from about 3.5 to about 8.0 and more preferably from about 5 to about 7.5.

The conditioning composition of the present invention optionally contains additional ingredients. For example, the conditioning composition may be formulated into a hair shampoo product, and then is

associated with nonionic, anionic, amphoteric and zwitterionic surfactants, well known in the art. Examples of anionic surfactants include sulfates such as alkyl sulfate, preferably containing 10-20 carbon atoms, (e.g., lauryl sulfate), alkyl ether sulfate, preferably containing 10-40 carbon atoms (e.g., lauryl ether sulfate), alkylamide sulfates preferably containing 10-20 carbon atoms, alkyl arylpolyether sulfate preferably containing 10-20 carbon atoms, monoglyceride sulfates; sulfonates, e.g. alkyl sulfonate, preferably containing 10-20 carbon atoms, alkylamide sulfonates, preferably containing 10-20 carbon atoms, alkylaryl sulfonates preferably containing 10-40 carbon atoms and  $\alpha$ -olefin sulfonates, preferably containing 10-20 carbon atoms; sulfosuccinic acid derivatives, e.g., alkyl ( $C_{10}$ - $C_{20}$ ) sulfosuccinates, alkyl ( $C_{10}$ - $C_{20}$ ) ether sulfosuccinates, alkyl ( $C_{10}$ - $C_{20}$ ) amide sulfosuccinates, and alkyl ( $C_{10}$ - $C_{20}$ ) amide polyether-sulfosuccinates; sarcosinates, e.g., ( $C_8$ - $C_{22}$ ) alkyl or ( $C_8$ - $C_{22}$ ) alkenyl sarcosinates; phosphate surfactants, e.g., alkyl ( $C_{10}$ - $C_{20}$ ) phosphates, or alkyl ( $C_{10}$ - $C_{20}$ ) ether phosphates, and the like. Examples of these ionic surfactants are described in U.S. Patent No. 4,419,344 to Strasella, et al., the contents of which are incorporated by reference. If present, these ionic surfactants are preferably present in amounts ranging from about 0.1% to 5% by weight and more preferably from about 0.1% to 2% by weight.

Examples of nonionic surfactants include fatty acid alkanolamides, e.g., mono or diethanolamine adduct (lauric diethanolamide, coconut diethanolamide), amine oxides, and ethoxylated nonionics, e.g., ethoxylated forms of alkylphenols, fatty alcohols, fatty esters, and mono and diglycerides, and the like; these examples all contain preferably 10-22 carbon atoms. These are described in Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 12, p. 887, John Wiley and Sons, Inc. 1994 and U.S. Pat. No. 4,954,335 to Janchipraponvej; the contents of which are incorporated by reference.

They are present in amounts ranging from 0.1% to about 5% by weight and more preferably from about 0.1 to about 2% by weight.

The amphoteric surfactants, also known as ampholytics, are both positively and negatively charged, and are usually derivatives of imidazolines or betaines, such as oleamidopropylbetaine and the like. They may also be associated with the homopolymer of the present invention in the hair conditioning compositions of the present invention. Sodium lauroamphoacetate may also be utilized in non-stinging shampoos. They are present in amounts ranging from about 0.1% to about 5% by weight and more preferably from about 0.1% to about 2% by weight.

Another optional ingredient in the composition includes a polyhydric compound. The polyhydric compound is present especially when the composition contains surfactants for it helps couple the homopolymers and the surfactant to provide a clear non-turbid aqueous-based hair conditioning composition. The polyhydric compound can be a glycol, a triol or polyol. Specific examples include, but are not limited to ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, glycerol or polyethylene or polypropylene glycol having an average molecular weight up to about 500. If present, it is present in amounts ranging from about 1% to about 20% by weight of the composition.

In addition, additives may also be optionally added to the compositions of the present invention, such as fragrances, dyes, hair colorants, dandruff control agents, hydrotropes, foam stabilizers, preservatives, (e.g., methyl and propyl parabens, DMDM hydantoin, diazolidinyl urea, imidazolidinyl urea, and the like), water softening agents, acids, bases, buffers and the like. These optional additives if present usually will be present in weight percentages of less than about 2% each, or from about 5% to about 10% by weight of the composition in

total.

The clean hair conditioning compositions of the present invention also may optionally include thickeners that are generally used in this art. Example includes sodium alginate, guar gum; xanthan gum; gum arabic, cellulose derivatives, such as methylcellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, and carboxymethylcellulose; and various polymeric thickeners, such as carboxyvinyl polymers, e.g., polyacrylic acid derivatives, and polyvinylalcohols and the like. These thickeners if present, are present in an amount ranging from about 0.1% to about 3%, and preferably from about 0.25% to about 1% by weight relative to the total weight of the composition.

Other optional materials include inorganic salts (e.g., alkali halides, sulfates or acetates, such as sodium, potassium, lithium, ammonium chloride, bromides, sulfates or acetates), humectants and similar material to provide esthetic properties and desirable physical properties to the composition. Preferably, such optional materials, if present, are present in weight percentages ranging from about 0.1% to about 10% each and from about 0.1% to about 20% in total, relative to the total weight, of the composition.

The composition of the present invention may be formulated into a solution, cream, spray, lotion or mousse, in accordance with procedures known to the skilled artisan. For example, if made into a spray, the composition is introduced to a suitable aerosol container; it is then pressurized with propellants.

In addition to personal care applications, the polymers of this invention may also be useful in detergent and/or cleaning compositions, e.g. in hard surface cleaners wherein the polymer may reduce deposition onto the hard surfaces.

All parts, percentages, ratios, averages, and the like expressed in this specification and the appended claims are by weight

unless otherwise apparent in context. All numerical values in the summary of the invention and the detailed description should be read once as modified by the term about, and then alternatively as not so modified. All numerical values in the appended claims should be read as  
5 modified by the term "about".

### Examples

### EXPERIMENTAL SECTION

#### 10 1. AMPHOTERIC MONOMER SYNHTESIS

Place dimethylaminopropylmethacrylamide (DMAPMA), 1723.8 g, in a reaction flask equipped with a condenser and an agitator and an air inlet. Purge air gently to the DMAPMA in the flask, and heat  
15 slowly to 50 ° C. Dissolve sodium monochloroacetate (SMCA), 1156.0 g, in demineralized water (1819.8 g) in a beaker. At 50° C and under air purging, add the SMCA aqueous solution to the DMAPMA in the reaction flask over one hour. Heat slowly to 60° C following the complete addition of SMCA solution, and hold at 60° C for two hours. Add demineralized  
20 water, 100.0 g, after cooling down the reaction mixture to room temperature. The resulting amphoteric monomer solution is slight orange of pH about 9.5 and of about 60% solids.

The pH of the monomer may also be adjusted with hydrochloric acid to about 7.5.

25

#### 2. HOMOPOLYMERIZATION

In a one-litre reaction flask, add demineralized water (384.0 g), the amphoteric monomer (pH 9.5, 52.6 g) and  
30 ethylenediaminetetraacetic acid, sodium salt (50%, 0.63 g). Under gentle nitrogen purging to the above mixture, heat to 80° C. At 80° C, add simultaneously but separately the initiator solution (2,2'-azobis(2-



amidinopropane) hydrochloride, trade-named as Wako V-50, 0.263 g in 81 g demineralized water), and the above amphoteric monomer (473 g). The addition time is three hours. Maintain the reaction temperature at 80° C throughout the addition. Hold at 80° C for one hour following the  
5 additions. Then add a second portion of the Wako V-50 initiator solution (0.19 g in 9.45 g water), and hold at 80° C for one hour. Cool the batch to room temperature. The viscosity at this stage was 24,000 cps at 34% solids.

The product was then adjusted to 30% solids by diluting  
10 with demineralized water. The viscosity at 30% solids was 8,800 cps (RV, 10 rpm, #5) and the pH was adjusted to 6.7.

### 3. EXAMPLES OF COPOLYMERIZATION

15 Put the following raw materials in a reaction flask: demineralized water (722.7 g), the above amphoteric monomer (211.1 g), vinyl pyrrolidone (VP, 62.8 g) and ethylenediaminetetraacetic acid, sodium salt (50%, 0.37 g). Under slow nitrogen purging, the above mixture was heated to 70° C. Added the initiator solution (Wako V-50,  
20 0.153 g in 2.9 g water) all at once when the temperature reached 70° C. Maintain the temperature at 70° C for three hours; periodic cooling was needed due to reaction exotherm. Heated the batch to 80° C and then added a second portion of Wako V-50 initiator (0.15 g in 1.0 g water). Maintained at 80° C for another hour. Cool the mixture to room  
25 temperature. The resulting polymer solution possesses the following properties:

- solids 20.3%
- viscosity (RV, #5, 10 rpm, 25° C) 32,000 cps
- pH 8.5

30

Under similar polymerization conditions, the above amphoteric monomer (labeled as AP) was copolymerizaing with

acrylamide (labeled as AM), dimethylaminopropylmethacrylamide, methyl chloride quaternary (labeled as MAPTAC), and dimethylaminopropylmethacrylamide, dimethylsulfate quaternary (labeled as MES). The results are shown below.

5

	<u>Copolymer</u>	<u>Molar Ratio</u>	<u>Solids</u>	<u>Viscosity</u>
				(RV, #5, 10 rpm, 25°C)
	VP-AP	1:1	20.3%	32,000 cps
10	VP-AP	7:3	20.7%	14,600 cps
	AM-AP	1:1	20.6%	51,600 cps
	MAPTAC-AP	1:1	34.3%	8,000 CPS
	MAPTAC-AP	1:2	34.5%	14,000 CPS
	MES-AP	1:1	20.8%	1125 CPS

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#### 4. EXAMPLES OF TERPOLYMERIZATION

To a one-litre reaction flask equipped with a condenser and an agitator, add the following raw materials:

20

- vinyl pyrrolidone (VP) 44.5 g
- amphoteric monomer (AP) 188.0 g
- vinyl acetate (VA) 17.2 g
- Demineralized water 630.1 g

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Under slow nitrogen purging, heat the mixture to 65° C. Add the initiator Wako V-50 solution (0.1 g in 2.0 g water) all at once at 65° C. Maintain the temperature at 65° C for three hours. The mixture will get viscous in about 20 minutes after the initiator added. A second portion of Wako V-50 initiator (0.02 g in 0.2 g water) is added then heat the batch to 30 90° C and maintain at 90° C for one hour. Cool the batch to room temperature. The viscosity of the finish product is 25,200 cps (LV, #3, 3 rpm, 25° C), and is of 19.1% solids and pH 4.4.

Under similar polymerization conditions but could differ in polymerization temperature and the amount of initiator, other examples of terpolymers with the above amphoteric monomer are made. The monomers used are:

- 5                   •vinyl pyrrolidone (VP)  
                   •acrylamide (AM)  
                   •dimethylaminopropylmethacrylamide, methyl chloride  
                   quaternary (MAPTAC)  
                   •dimethylaminopropylmethacrylamide, dimethylsulfate  
 10   quaternary (MES)  
                   •dimethylaminopropylmethacrylamide, N-(3-chloro-2-  
                   hydroxypropyl)trimethylammonium chloride quaternary (diquat)  
                   •2-acrylamido-2-methylpropanesulfonic acid, potassium salt  
                   (K-AMPS)  
 15                   •methacrylic acid esterified with behenyl alcohol ethoxylates  
                   (25 moles of ethylene oxide) (BEM)

The results are exemplified below:

20	<u>Terpolymer</u>	<u>Molar Ratio</u>	<u>% Solids</u>	<u>Viscosity</u>
			(LV, #3 or #4, 25°C)	
	VP-AP-VA	4:4:2	19.1%	25,200 cps
	VP-AP-VA	4:4:2	19.2%	23,000 cps
25	VP-AP-MAPTAC	4:4:2	20.1%	2,200 cps
	VP-AP-MES	5:3:2	20.7%	2,300 cps
	VP-AP-Diquat	5:3:2	21.2%	10,800 cps
	VP-AP-Diquat	5:3:2	21.7%	27,500 cps
	AM-AP-MES	1:1:1	20.6%	7,200 cps
30	VP-AP-Diquat	5:3:2	20.9%	17,000 cps
	VP-AP-MES	5:3:2	20.9%	17,000 cps

	VP-AP-Diquat	5:3:2	21.2%	32,000 cps
	VP-AP-MES	5:3:2	21.3%	30,000 cps
	AM-AP-MES	1:1:1	21.0%	20,000 cps
	VP-AP-K-AMPS	2:2:1	20.9%	430 cps
5	VP-AP-BEM	49.25:50.25:0.5	21.6%	1,625 cps
	AM-AP-BEM	49.25:50.25:0.5	22.2%	3,325 cps

#### 5. COMPATIBILITY OF ANIONIC SURFACTANTS

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#### POLYMER DOSAGE AND SURFACTANT SYSTEMS

<i>POLYMER</i>	<i>---0.3% ACTIVE IN 10% SLES- EO2</i>	<i>---0.3% ACTIVE IN 12% MPC</i>	<i>---0.5% ACTIVE IN 10% ALS</i>
VP:AP:MAPTAC 4:4:2	clear	clear	clear
VP:AP:MES 5:3:2	clear	clear	clear
AM:AP:MES 1:1:1	cloudy	cloudy	cloudy
VP:AP:DIQUAT 6:4:1	clear	clear	insoluble
VP:AP:DIQUAT 5:3:2	cloudy	cloudy	clear
HOMOPOLYMER OF AP	clear	clear	clear
AP:MAPTAC 2:1	clear	cloudy	cloudy(ppt)
AP:MAPTAC 1:1	cloudy	cloudy(ppt)	cloudy(ppt)
VP:AP:VA 4:4:2	clear	slight haze	clear

SLES-EO2 is sodium lauryl ether sulfate (2 mole ethylene oxide) Rhodapex ES2.

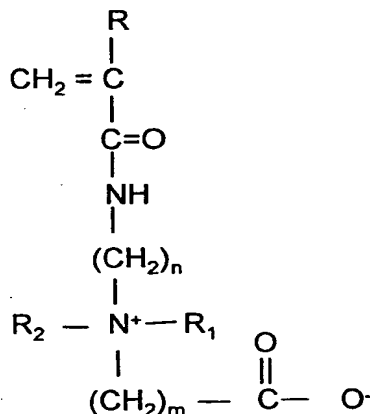
15

MIRACARE™ MPC is a multi-purpose concentrate for various personal care applications.

ALS is ammonium lauryl sulfate, Rhodapon L22/C.

**What is claimed is:**

1. A monomer having the formula:



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wherein:

R is hydrogen or C<sub>1</sub> to C<sub>4</sub> alkyl;

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R<sub>1</sub> and R<sub>2</sub> are independently C<sub>1</sub> to C<sub>18</sub> alkyl;

n is independently 2 to 10, typically 2, 3, or 4; and m is 1 to 10, typically 1, 2, 3 or 4.

- 15 2. A monomer as claimed in claim 1 wherein R is methyl or hydrogen.  
 3. A monomer as claimed in claim 1 wherein R is methyl.  
 4. A monomer as claimed in claim 1 wherein R is hydrogen.  
 5. A monomer as claimed in claim 1 wherein R<sub>1</sub> and R<sub>2</sub> are independently methyl or ethyl.  
 20 6. A monomer as claimed in claim 1 wherein R<sub>1</sub> and R<sub>2</sub> are both methyl.  
 7. A monomer as claimed in claim 1 wherein n is 2, 3, or 4.  
 8. A monomer as claimed in claim 1 wherein m is 1, 2, 3 or 4.

9. A monomer as claimed in claim 1 wherein  $R_1$  and  $R_2$  are both methyl,  $n$  is 2 and  $m$  is 1.
10. A monomer as claimed in claim 9 wherein  $R$  is methyl.
11. A monomer as claimed in claim 9 wherein  $R$  is hydrogen.
- 5 12. A homopolymer of a monomer of claim 1.
13. A homopolymer of a monomer of claim 10.
14. A copolymer of a monomer of claim 1 and at least one other monomer
15. A copolymer of a monomer of claim 10 and at least one other monomer.
- 10 16. A personal care composition comprising a member selected from the group consisting of a homopolymer of a monomer as claimed in claim 1, and copolymers comprised of a monomer as claimed in claim 1 and at least one other monomer.
17. A personal care composition comprising a member selected from the
- 15 group consisting of a homopolymer of a monomer as claimed in claim 10, and copolymers comprised of a monomer as claimed in claim 10 and at least one other monomer.
18. A personal care composition as claimed in claim 16 wherein said composition is a shampoo wherein an anionic surfactant is present in
- 20 said composition.
19. A personal care composition as claimed in claim 17 wherein said composition is a shampoo wherein an anionic surfactant is present in
- said composition.
20. A personal care composition as claimed in claim 16 wherein said
- 25 composition is a hair conditioner composition.
21. A personal care composition as claimed in claim 17 wherein said composition is a hair conditioner composition.
22. A personal care composition as claimed in claim 16 wherein said composition is a skin moisturizing composition.

23. A personal care composition as claimed in claim 17 wherein said composition is a skin moisturizing composition.
24. A personal care composition as claimed in claim 16 wherein said composition is a skin cleanser.
- 5 25. A personal care composition as claimed in claim 17 wherein said composition is a skin cleanser.
26. A method of using a personal care composition as claimed in claim 16 comprising contacting a member selected from the group consisting of skin and hair with said composition.
- 10 27. A method of using a personal care composition as claimed in claim 17 comprising contacting a member selected from the group consisting of skin and hair with said composition.
28. A method of making a personal care composition comprising incorporating therein a member selected from the group consisting of
- 15 a homopolymer of a monomer as claimed in claim 1, and copolymers comprised of a monomer as claimed in claim 1 and at least one other monomer.
29. A method of making a personal care composition comprising incorporating therein a member selected from the group consisting of
- 20 a homopolymer of a monomer as claimed in claim 10, and copolymers comprised of a monomer as claimed in claim 10 and at least one other monomer.
30. A detergent composition comprising a member selected from the group consisting of a homopolymer of a monomer as claimed in claim
- 25 1, and copolymers comprised of a monomer as claimed in claim 1 and at least one other monomer.
31. A detergent composition comprising a member selected from the group consisting of a homopolymer of a monomer as claimed in claim
- 30 10, and copolymers comprised of a monomer as claimed in claim 10 and at least one other monomer.

32. A method of using a detergent composition as claimed in claim 30 comprising contacting a hard surface with said composition.

33. A method of using a detergent composition as claimed in claim 31 comprising contacting a hard surface with said composition.

5 34. A method of making a detergent composition comprising incorporating therein a member selected from the group consisting of a homopolymer of a monomer as claimed in claim 1, and copolymers comprised of a monomer as claimed in claim 1 and at least one other monomer.

10 35. A method of making a detergent composition comprising incorporating therein a member selected from the group consisting of a homopolymer of a monomer as claimed in claim 10, and copolymers comprised of a monomer as claimed in claim 10 and at least one other monomer.

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# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 99/19801

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C07C233/36 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US KAWAMUKAI, HIROSHI ET AL: "Hydrophilic polymers and cosmetic moisturizers containing them" retrieved from STN Database accession no. 131:23268 XP002124234 See RN 79702-44-6, 226698-74-4 and 83623-26-1. abstract &amp; JP 11 130822 A (KAO CORP., JAPAN) 18 May 1999 (1999-05-18)</p> <p style="text-align: center;">-/-</p>	1-11, 14, 15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

17 December 1999

Date of mailing of the international search report

11/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3018

Authorized officer

Arias-Sanz, J

# INTERNATIONAL SEARCH REPORT

b International Application No

PCT/US 99/19801

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>DATABASE CHEMABS 'Online!            CHEMICAL ABSTRACTS SERVICE, COLUMBUS,            OHIO, US            OOMURA, TAKAYUKI: "Hair-setting            compositions"            retrieved from STN            Database accession no. 129:293670            XP002124235            See RN 122273-40-9            abstract            &amp; JP 10 245325 A (SHISEIDO CO., LTD.,            JAPAN) 14 September 1998 (1998-09-14)</p>	<p>1-3,            5-10,14,            15</p>
X	<p>HAHN, MATHIAS ET AL: "Synthesis and            Properties of Ionically Modified Polymers            with LCST Behavior"            MACROMOLECULES 5616-5623,            vol. 31, no. 17,            - 8 June 1998 (1998-06-08) pages            5616-5623, XP002124233            See RN 80921-09-1</p>	<p>1-3,            5-10,14,            15</p>
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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/19801

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US SASAKI, HIROSHI ET AL: "Hair preparations containing amphoteric surfactants, polyoxyalkylene alcohol ethers and cationic compounds" retrieved from STN Database accession no. 127:39469 XP002124237 See RN 122273-40-9 abstract &amp; JP 09 100216 A (SHISEIDO CO., LTD., JAPAN) 15 April 1997 (1997-04-15)</p>	1-35
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